



Photocatalytic Degradation of Dichlorvos using Graphite Oxide Based Catalysts

T. Rajachandrasekar¹, P. Selvakumar², K. Balakrishnan^{3*}

¹Department of Chemistry, M. R. Govt. Arts College, Mannargudi, India.

²Department of Chemistry, SIVET College, Tambaram, Chennai, India.

³Department of Chemistry, AVVM Sri Pushpam College, Poondi, India.

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Abstract

Graphite oxide (GO) is a p-type semiconductor prepared from graphite. It shows different properties than the other carbon allotropes. GO has more no of oxygen containing functional groups and has higher surface area. To harvest these properties, different semiconductor like TiO₂ and WO₃ were introduced into GO by photo deposition to prepare GO-TiO₂ and GO-WO₃ couple semiconductors respectively. Materials obtained were characterized by different techniques such as XRD, DRS UV, FTIR and TEM. To find out their photocatalytic ability, degradation of Dichlorvos, a model organochlorine as well as organophosphorous compound was carried out in aqueous suspension under visible light. The photocatalytic activity was correlated with various structural and chemical changes in graphite oxide due to the introduction of titania and tungsten trioxide. From the results it was observed that introduction of titania as well as tungsten trioxide greatly enhanced the photocatalytic activity of graphite oxide towards degradation of Dichlorvos. Among these two, GO-TiO₂ was found to be highly active and showed complete degradation under visible light irradiation.

Keywords: Dichlorvos; Degradation; Graphite oxide; Photocatalyst.

1. INTRODUCTION

The environment and everything connected with it is being continuously contaminated by domestic and industrial pollutants. Uncontrolled growth of population and industries have significantly altered the environment and reduced the natural resources. Removal of persistent and toxic organic substrates present in waste water effluent becomes the prime task for scientists and governments. The already existing methods like adsorption or biological treatment appear to have many drawbacks since the former involves only phase transfer of the pollutants and the latter cannot be applied to contaminants which are toxic to the bacteria. Semiconductor assisted photocatalysis is a promising environmentally benign process which has been widely and effectively used for the removal of pollutants (Hoffmann *et al.* 1995). Since charge separation determines the effectiveness of semiconductor photocatalysis, coupled semiconductor could be the opt

route to increase the charge separation than the other semiconductor system (Sekulic *et al.* 2004). Although many coupled semiconductors have been tried, the p-n junction constructed by coupling p-type graphite oxide semiconductor with an n-type could be an alternate for photocatalysis.

Graphite oxide is produced by the oxidation of graphite which bears oxygen functional groups in basal plane and sheet edges of GO make it strongly hydrophilic, which allows it to readily swell and disperse in water (Lerf *et al.* 1998). However, graphite oxide has these advantageous, it failed to perform the effective oxidation of organic compounds due to its lower oxidation potential. However, this can be overcome by combining GO with n-type semiconductors. Among many n-type semiconductors, TiO₂ and WO₃ have been used widely due to their higher oxidation potential and chemical stability. Recently, efforts have been taken to synthesize

*K. Balakrishnan Tel. no: +91 9498174672
Email: balki63@gmail.com

GO-TiO₂ coupled semiconductors by different routes such as hydrothermal (Hao Zhang *et al.* 2010) photo deposition (Graeme Williams *et al.* 2008) and electrochemical (He Yunqie *et al.* 2010) methods. Photocatalytic tests using GO-TiO₂ have been performed for the degradation of organic pollutant (Zhang Qiong *et al.* 2010), degradation of E. Coli. (Akhavan and Ghaderi, 2010) and water splitting. Among the preparation methods, photodeposition have advantages such as reduction of GO can be controlled (Graeme Williams *et al.* 2008), preparation time is much faster and no hazardous chemicals involved. From the literatures cited, it was found that GO-TiO₂ and GO-WO₃ synthesized by photodeposition method is not yet used for the degradation of Dichlorvos. Dichlorvos (DDVP) an insecticide is used widely for crop protection mainly in greenhouses and for controlling parasites and insects in houses, aircraft, and outdoor areas (as aerosols, liquidsprays). Dichlorvos is highly toxic by inhalation, dermal absorption, and ingestion. EPA has classified dichlorvos as a Group B2, probable human, carcinogen. Hence, In this work, GO-TiO₂ and GO-WO₃ coupled semiconductors with 1:1 ratio were synthesized by photodeposition method using commercial sample of P-25 titania and tungsten trioxide respectively and tested for the photocatalytic degradation of Dichlorvos.

2. EXPERIMENTAL

2.1 Material synthesis

The detailed synthesis procedure for pure GO was followed as in the literature (Yeh *et al.* 2010). The coupled semiconductor material was synthesized by adding 1 g of WO₃ or TiO₂ to the 1000 mL solution containing 1 g of dry weight of pure GO in order to prepare coupled semiconductor with 1:1 ratio. The whole solution was irradiated for 2 hrs under visible light. The irradiated sample then filtered and dried at 323 K for 24 hrs. The sample was then ground for further use.

2.2 Catalysts characterization

High-resolution transmission electron microscopy (HRTEM; JEOL, Japan) was used to explore the microstructure of the GO coupled semiconductor specimens. The samples for HRTEM analysis were prepared by placing a drop of a GO coupled semiconductors/ethanol solution on a carbon film-coated grid. The crystal structure of the samples was characterized by powder X-ray diffraction (XRD) using a Phillips X'pert model diffractometer with Cu-K α radiation. Fourier-transform infrared (FTIR)

spectroscopy in diffuse reflectance mode was conducted using a JASCO FTIR-4100 (Japan) spectrometer. To obtain the UV-vis absorption spectra, the coupled semiconductors/water solutions were placed in a 1^{cm} quartz cuvette and analyzed using Shimadzu UV2450 model spectrophotometer.

2.3 Photocatalytic activity

Photocatalytic reaction was carried out in an inner irradiation type photocatalytic reactor. The light source was 400 W high pressure mercury lamp. The temperature of reaction vessel was maintained at 18 °C by filling with flowing thermo stated cooling water. 1 M NaNO₂ aqueous solution was used to filter out the UV light. External oxygen was fed by purging air. The reactor set-up was covered with aluminium foil followed by a black cloth to prevent UV light leakage. 100 mL of 100 ppm DDVP taken and stirred for 30minutes to attain adsorption – desorption equilibrium then it was irradiated. The sample was collected at the interval of every one hour and filtered through 0.2 μ m filter. DDVP concentration was analyzed by HPLC (Shimadzu V_{CPN}), in which a C-18 column was employed and a mobile phase of acetonitrile/water (60:40, v/v) was used at a flow rate of 1.0 mL/min. An injection volume of 20 μ L was used and the amount was determined by a UV detector. Extent of mineralization was measured by TOC analyser (Shimadzu, TOC V_{CPN}, Japan) by catalytic oxidation method (platinum was used as catalyst).

3. RESULTS & DISCUSSION

3.1 Physico-Chemical characterizations

Fig. 1 shows the XRD patterns of GO-TiO₂ and GO-WO₃. Both catalyst does not show corresponding GO peak and only peaks of WO₃ and TiO₂ have appeared. The XRD pattern of GO-TiO₂ is the typical of commercial P-25 titania in which anatase and rutile phases are composed as 75:25. The presence of rutile phase is found at 2 theta value of 27.3 and the remaining peaks are corresponding to anatase. The high intensity peak shown at 25.3 is corresponding to 101 plane of anatase titania. All of the reflection patterns of the WO₃ could be indexed to a monoclinic phase (JCPDS 72-1465). The regular stack of GO might have been broken by exfoliation and hence the diffraction peak is disappeared in both the catalysts (Cai and Song, 2007). Therefore, we assumed that the formed metal oxides through this process might attach onto these carbon sheets and prevent the aggregation and restack of these as-synthesized graphene sheets, which weakens the diffraction of single layered carbon sheets consequently.

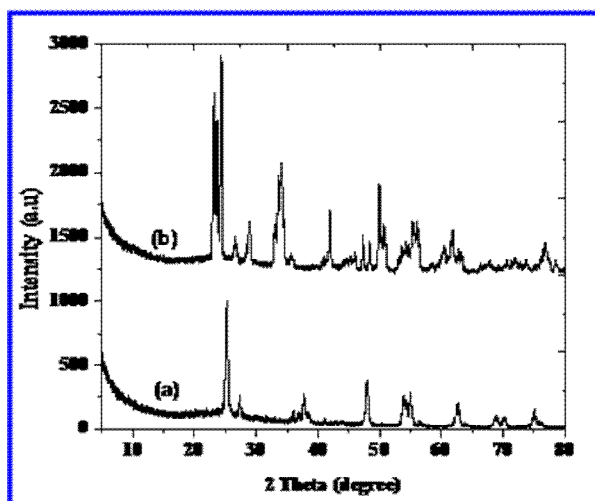


Fig. 1: X-Ray Diffraction patterns of (a) GO-TiO₂ and (b) GO-WO₃

In all the FTIR spectra (Fig. 2 a-c), a peak is observed at 3200-3500 cm⁻¹ corresponding to O-H stretching frequency (Paredes *et al.* 2008) and this particular peak is broader in pure GO (Fig. 2c). In GO-TiO₂ as well as GO-WO₃, this peak is reduced as a result of modification of -OH groups. This is supported

by the fact that GO-TiO₂ and GO-WO₃ samples are appeared as somewhat dry, where as pure GO contains moisture in it. The epoxide group is observed at 970 cm⁻¹ in all the FTIR spectra. The absorption corresponding to C=C in both GO-TiO₂ and GO-WO₃ is observed at around 1570 cm⁻¹ which is due to reduction of GO during irradiation (Trick and Saliba, 1995). The stretching frequency of C=O is found at 1690 cm⁻¹ in GO-TiO₂ and 1720 cm⁻¹ in GO-WO₃. The peak corresponding to C=O in GO-TiO₂ is shifted to lower frequency reveals that the carboxylic group is modified as ester type link as reported earlier for graphene-C₆₀ (Xiaoyan Xiang *et al.* 2009). The tertiary alcoholic group is detected at 1390 cm⁻¹ in all the catalysts (Lucas *et al.* 1995). The peak for phenolic O-H is observed in GO-WO₃ and pure GO at 1230 cm⁻¹. The phenolic O-H might have reacted with TiO₂ and hence this particular peak is disappeared in GO-TiO₂. The band at 750 cm⁻¹ in GO-WO₃ is assigned to a W-O vibration of surface tungstate species (Boyse and Ko, 1991), where as the peak for W-O-W is observed at 858 cm⁻¹ (Wachs, 1996). The presence of titanium is observed from the FTIR peak at 476 cm⁻¹ for Ti-O bonding (De *et al.* 2002).

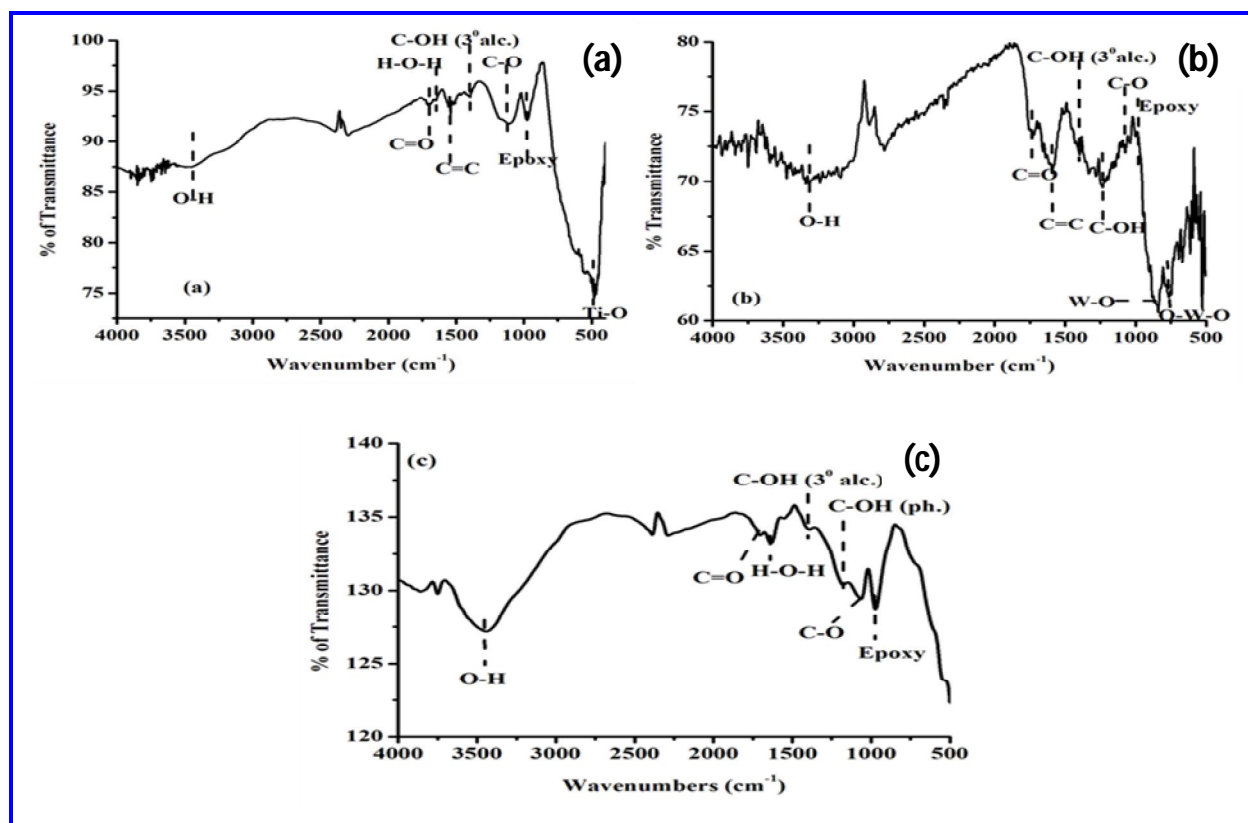


Fig. 2: FTIR spectra of (a) GO-TiO₂ (b) GO-WO₃ and (c) GO

Fig. 3 shows the lower magnification TEM images of (a) GO-WO₃ and (b) GO-TiO₂. In both the images, graphene nanosheets were observed to be of wrinkled silk veil like that were ribbed and rolled are inherent to graphene nanosheets (Meyer *et al.* 2007). The rolling structure found at the rim of GO caused by uneven stress indicates that the formed GO is very thin. From fig. 3 (a-b), it can be clearly seen that the GO sheet was decorated with TiO₂ nano particles in GO-TiO₂ and few particles with large size in GO-WO₃ respectively. Due to the smaller size of titania, they entered into inside of interlayer. There are two kinds of particles seen in the figure. brighter one is lies on the surface of GO sheet and darker one is lies below the sheet. This kind of observation has also been observed for Co₃O₄ particles in GO (Chao Xu *et al.* 2008).

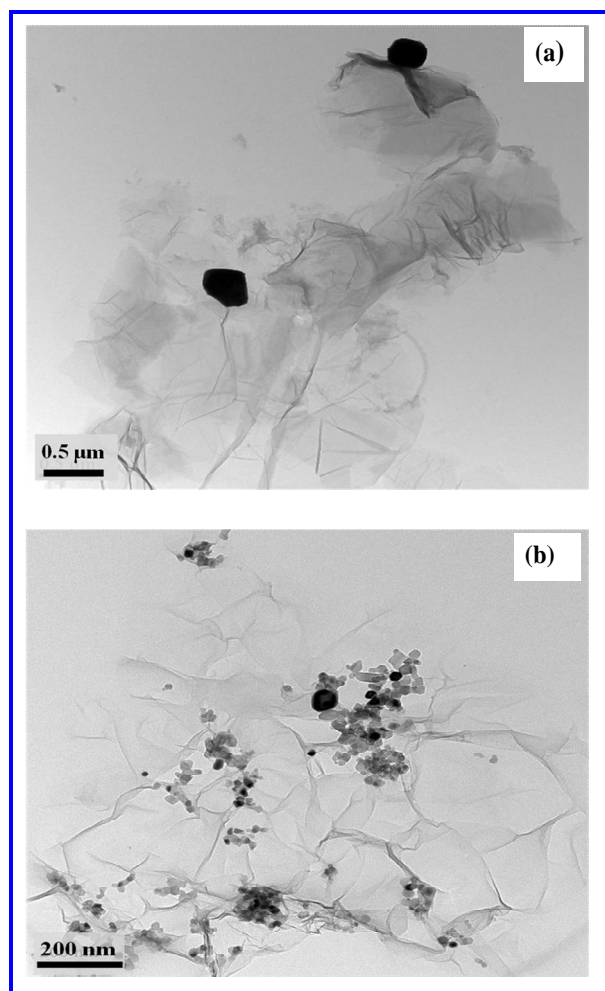


Fig. 3: Low magnification TEM images of (a) GO-WO₃ (b) GO-TiO₂

This might have occurred due to the presence of epoxy and hydroxyl functional groups on both sides

of GO. The sheet edge is found to be very thick in GO-WO₃ which may be due to restacking of sheets (fig. 3a). Carboxyl groups at the sheet edges might have reacted and hence restacking taken place. However, in GO-TiO₂, carboxyl groups are utilized for bonding which restricted the restacking.

Fig. 4a & 4b represents the UV-Visible absorption spectra of GO-TiO₂ and GO-WO₃. Analysis was carried out in liquid form by taking catalysts in water. As seen from the spectra, the absorption onset for GO-TiO₂ was found to be 425 nm while P-25 absorption was at 390 nm. GO-WO₃ showed two absorption, one is at 384 nm and another is at 581 nm. Absorption onset for WO₃ is 380 nm which is found to be unaffected in GO-WO₃. The absorption onset at 581 is due to GO material (Yeh *et al.* 2010). The increase in absorption onset from 390 to 425 nm in GO-TiO₂ might be due to coupling of TiO₂ with GO.

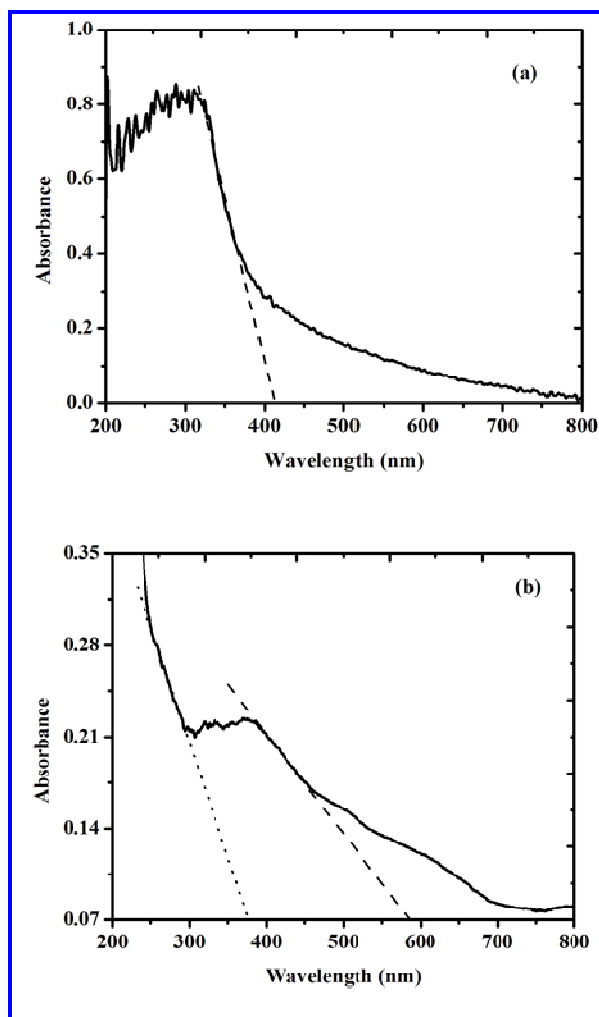


Fig. 4: UV-Visible absorption spectra of (a) GO-TiO₂ and (b) GO-WO₃

3.2 Photocatalytic activity

Catalyst concentration of 100 mg/L and reactant concentration of 100 ppm were chosen as the optimized condition for the photocatalytic activity. The concentration remained after attaining adsorption-desorption equilibrium was taken as the initial concentration for plotting the results.

3.2.1 Effect of different GO based coupled semiconductors

Fig. 5 shows the Dichlorvos degradation profile using different catalysts under visible light. From the figure, it is found that the increase in reaction time increased the activity of all the catalysts except GO. The degradation activity of different catalysts follows the trend: $\text{GO-TiO}_2 > \text{GO-WO}_3 > \text{WO}_3 > \text{TiO}_2 > \text{GO}$. GO-TiO_2 showed the fastest as well as complete degradation. The next highly active catalyst is GO-WO_3 . On comparing GO-WO_3 with GO-TiO_2 , latter is the highly active one. However on comparing TiO_2 and WO_3 , latter found to be highly active. This is because WO_3 has higher oxidation potential as well as absorption lies at longer wavelength than TiO_2 and it leads to higher activity of WO_3 . Since TiO_2 and WO_3 have lowest surface area, they failed to show significant increase in adsorption as well as photocatalytic degradation.

As seen from the characterization results, GO-TiO_2 have lowest crystallite size and shorter wavelength of absorption. Former enhances the adsorption and latter paves way for effective harvesting of visible light. UV-Visible absorption spectroscopy showed single absorption in GO-TiO_2 due to coupling of GO and TiO_2 . GO-WO_3 showed two absorptions corresponding to WO_3 and GO at 384 and 581 nm respectively. This formation of covalent linkage between TiO_2 and GO is also observed from the FTIR results. The peak corresponding to C=O is shifted to lower frequency and peak for phenolic O-H is not observed in GO-TiO_2 . However, high levels of covalent bonding of WO_3 particles are not observed in GO-WO_3 and they present as aggregated particles. When they taken in aqueous medium under irradiation, some of the WO_3 particles may release from the surface of GO and present as isolated species which is confirmed by UV analysis. Consequently, in GO-WO_3 the degradation occurs on two species that are WO_3 and GO-WO_3 . Hence recombination possibility is more in GO-WO_3 . The TEM results also show that TiO_2 particles are well dispersed on GO sheets and covalently bonded through functional group which promotes effective charge separation. Due to these reasons, GO-TiO_2 showed higher activity than GO-WO_3 .

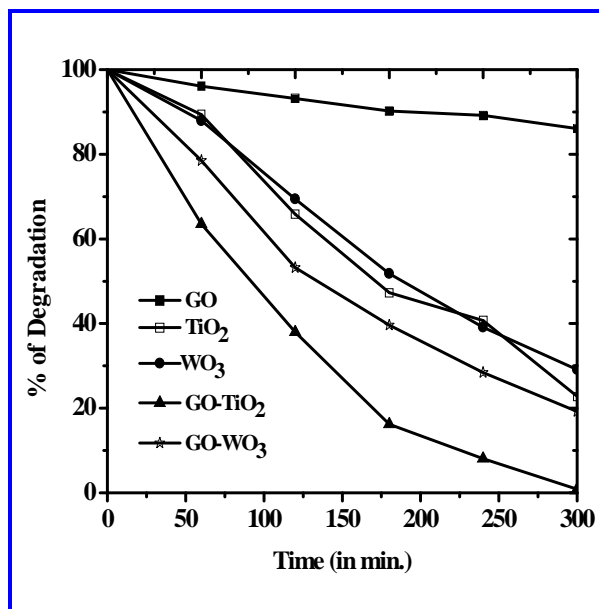


Fig. 5: Degradation profile of Dichlorvos on different catalysts

From the results, it is defended that GO-TiO_2 is highly active due to effective charge separation. In a p-n junction type coupled semiconductor, the conduction band electron of p-type can migrate to conduction band of n-type and then the electron will reduces the oxygen. As a result, the superoxide ion, a strong oxidizing agent will be formed. The hole from n-type will transfer to p-type and increases the hole accumulation in valence band of p-type where hydroxide ion will be oxidized to hydroxide radical. Due to these processes, pollutant is degraded in two ways i.e by superoxide ion and hydroxide radical. To support this, reaction was conducted in both presence and absence of Air. Fig. 6 shows the results of influence of external oxygen. As revealed in the fig., introduction of external oxygen does not influence much on the photocatalytic degradation ability of GO-WO_3 . However, it influenced much in the case of GO-TiO_2 . In GO-TiO_2 , GO has higher reduction potential and TiO_2 has higher oxidation potential. GO-TiO_2 linked via covalent bonds. Hence, the oxidation of Dichlorvos taken place via both oxidations by hole as well as by superoxide ion. This improved the photocatalytic activity of GO-TiO_2 . When we see to the activity profile of GO-WO_3 , it doesn't show any significant increase in activity due to external oxygen as it is not perfectly coupled or they are covalently bound. Hence, the effective charge transport is not possible and electron received at conduction band of GO is not sufficient to reduce oxygen in the case of GO-WO_3 .

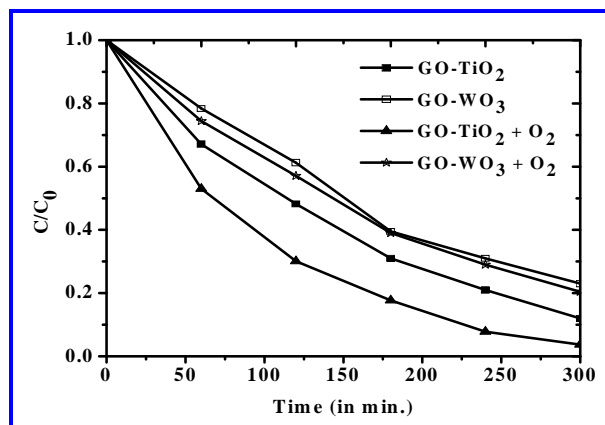


Fig. 6: Influence of air purging on degradation of Dichlorvos on different catalysts

4. CONCLUSION

The p-n junction type materials such as GO-TiO₂ and GO-WO₃ were synthesized by photodeposition method using commercial TiO₂ and WO₃ respectively. Materials synthesized were characterized by different physico-chemical techniques. These materials then tested for the photocatalytic degradation of Dichlorvos. Characterization results showed that more number of TiO₂ particles are present at both inside the GO layer due to smaller size and also covalently bound through oxygen functional groups on basal planes and sheet edges. However, lesser amount of WO₃ particles are deposited on GO and that too as agglomerated which make it fail to perform effective charge transfer. These were confirmed with UV-Visible spectra, FTIR and TEM analysis. Hence, GO-TiO₂ showed higher activity than GO-WO₃. Coupled semiconductor materials showed higher activity than their individual counterparts. This is due to the effective transfer of charge carrier in coupled semiconductors. The influence of external oxygen was tested by purging oxygen during reaction. Due to larger amount of TiO₂ particles covalently bound with GO, the effective charge transport taken place and it showed increase in activity in presence of external oxygen, while GO-WO₃ doesn't influence in anyway. This study put forth a conclusion from the results obtained that GO based coupled semiconductors could be the better candidate to enhance the photocatalytic degradation towards organic pollutants under visible light irradiation.

REFERENCES

Akhavan, O. and Ghaderi, E., Photocatalytic reduction of graphene oxide nanosheets on TiO₂ thin film for Photo inactivation of bacteria in solar light irradiation, *J. Phys. Chem. C*, 113(47), 20214-20220(2009).
doi:10.1021/jp906325q

Boyse, R. A. and Ko, E. I., Crystallization behavior of tungstate on zirconia and its relationship to acidic properties, *J. Catal.*, 171(1), 191-207(1997).
doi:10.1006/jcat.1997.1761

Cai, D. and Song, M., Preparation of fully exfoliated solvents graphite oxide nanoplatelets in organic, *J. Mater. Chem.*, 17(35), 3678-3680(2007).
doi:10.1039/B705906J

Chao Xu, Xin Wang, Junwu Zhu, Xuejie Yang, Lude Lu, Deposition of Co₃O₄ nanoparticles onto exfoliated graphite oxide sheets, *J. Mater. Chem.*, 18(46), 5625-5629(2008).
doi:10.1039/b809712g.

Graeme Williams, Brian Seger and Prashant V. Kamat, TiO₂-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide, *ACS Nano.*, 2(7), 1487-1491(2008).
doi:10.1021/nn800251f

Hao Zhang, Xiaojun Lv, Yueming Li, Ying Wang, Jinghong Li, P25-Graphene composite as a high performance photocatalyst, *ACS Nano*, 4(1), 380-386(2010).
doi:10.1021/nn901221k

He Yunqiu, Wang Ruihua, Zhang Qiong, Chen Xiaogang, LiLinjiang, Hu Donghu, Synthesis of TiO₂/GO composite film via an electrochemical route, *J. Nanosci. Nanotechnol.*, 10 (11), 7097-7102(6)(2010).
doi:10.1166/jnn.2010.2771

Hoffmann, M. R., Martin, S. T., Choi, W. and Bahnemann, D. W., Environmental applications of semiconductor photocatalysis, *Chem. Rev.*, 95(1), 69-95(1995).
doi:10.1021/cr00033a004

Lerf, A., He, H., Forster, M. and Klinowski, J., Structure of Graphite Oxide revisited, *J. Phys. Chem. B.*, 102(23), 4477-4482(1998).
doi:10.1021/jp9731821

Lucas, C. H., López-Peñado, A. J., López-González, J. de D. and Martín-Aranda, R. M., Study of oxygen-containing groups in a series of graphite oxides: Physical and chemical characterization, *Carbon*, 33(11), 1585-1592(1995).
doi:10.1016/0008-6223(95)00120-3

Meyer, J. C., Geim, A. K., Katsnelson, M. I., Novoselov, K. S., Booth, T. J. and Roth, S., The structure of suspended graphene sheets, *Nature*, 60-63, 446 (2007).
doi:10.1038/nature05545

Paredes, J. I., Villar-Rodil, S., Martínez-Alonso, A., Tasco'n, J. M. D., Graphene oxide dispersions in organic solvents, *Langmuir*, 24(19), 10560-10564(2008).
doi:10.1021/la801744a

- Sekulic, J., Magraso, A., Ten Elshof, J. E. and Blank, D. H. A., Synthesis and characterization of microporous titania membranes, *J. Sol-Gel Sci. Technol.*, 31(1), 201-204(2004).
[doi:10.1023/B:JSST.0000047987.50901.15](https://doi.org/10.1023/B:JSST.0000047987.50901.15)
- Soler-Illia, G. J. de A. A., Louis, A. and Sanchez, C., Synthesis and characterization of mesostructured titania-based materials through evaporation-induced self-assembly, *Chem. Mater.*, 14(2), 750-759(2002).
[doi: 10.1021/cm011217a](https://doi.org/10.1021/cm011217a)
- Trick, K. A. and Saliba, T. E., Mechanisms of the pyrolysis of phenolic resin in a carbon/phenolic composite, *Carbon*, 33(11), 1509-1515(1995).
[doi:10.1016/0008-6223\(95\)00092-R](https://doi.org/10.1016/0008-6223(95)00092-R)
- Wachs, I. E., Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts, *Catal. Today.*, 27(3-4), 437-455(1996).
[doi:10.1016/0920-5861\(95\)00203-0](https://doi.org/10.1016/0920-5861(95)00203-0)
- Xiaoyan Zhang, Yi Huang, Yan Wang, Yanfeng Ma, Zunfeng Liu, Yongsheng Chen, Synthesis and characterization of a graphene-C₆₀ hybrid material, *Carbon*, 47(1), 334-337(2009).
[doi:10.1016/j.carbon.2008.10.018](https://doi.org/10.1016/j.carbon.2008.10.018)
- Yeh, T. F., Syu, J. M., Cheng, C., Chang, T. H. and Teng, H., Graphite oxide as a photocatalyst for hydrogen production from water, *Adv. Funct. Mater.*, 20(14), 2255-2262(2010).
[doi:10.1002/adfm.201000274](https://doi.org/10.1002/adfm.201000274)
- Zhang, Q., He, Y. Q., Chen, X. G., Hu, D. H., LI, L. J., Yin, T. and Ji, L. L., Intercalated structure and photocatalytic properties of TiO₂- graphite oxide composite, *Acta Physico-Chimica Sinica*, 26(3), 654-662(9)(2010).
- Zhang, X. Y., Li, H. P. and Cui, X. L., Preparation and Photocatalytic Activity for Hydrogen Evolution of TiO₂/Graphene Sheets Composite, *Chine. J. Inorg. Chem.* 11, 1903-1907(2009).